Supporting Information

Polymer Grafted Porous Silica Nanoparticles with Enhanced CO₂

Permeability and Mechanical Performance

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Experimental Section

Materials.

Monomers: methyl methacrylate (MMA, 99%, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, $M_n \sim 300$, Sigma-Aldrich) were purified by passing through a column filled with alumina to remove the inhibitor. Tris(2-dimethylaminoethyl)amine (Me₆TREN, 99%, Alfa), tetrahydrofuran (THF, 99%, VWR), anisole (99%, Aldrich), ethyl acetate (99%, Aldrich), 1-butyl imidazole (98%, Aldrich), lithium bis-(trifluoromethanesulfonyl)imide (LiTf₂N, >99%, Aldrich), butyronitrile (BuCN, 99%, Aldrich), vinylbenzyl chloride (90%, Aldrich), methanol (99%, VWR), hexane (99%, VWR), acetone (99%, VWR), N,N-dimethylformamide (DMF, 99%, VWR), ethyl α-bromoisobutyrate (EBiB, 98%, Sigma-Aldrich), copper(II) bromide (CuBr₂, 99%, Aldrich), tin(II) 2-ethylhexanoate (Sn(EH)₂, 95%, Aldrich), 48% hydrofluoric acid aqueous solution (HF, >99.99% purity, Aldrich), ammonium hydroxide aqueous solution (NH₄OH, 28.0-30.0%, Fisher), anhydrous magnesium sulfate (MgSO₄, Fisher), allyl alcohol (99%, Aldrich), triethylamine (TEA, 99.5%, Aldrich), 2-bromoisobutyryl bromide (2BiB, 98%, Aldrich), platinum(0)-1,3-divinyl-1,1,3,3- tetramethylsiloxane complex in xylene (Karstedt's catalyst, 2% Pt, Aldrich), chlorodimethylsilane (98%, Aldrich), triethoxysilane (95%, Aldrich), hexamethyldisilazane (HMDZ, 99%, Aldrich) were used as received without further purification. Hollow silica nanoparticles were prepared following previously reported procedures.¹ Silica nanoparticles, 30 wt% solutions in methyl isobutyl ketone (MIBK-ST), effective diameter $d \approx 15.8$ nm, were kindly donated by Nissan Chemical Corp. and used as received. The tetherable ATRP initiator 3-(chlorodimethylsilyl)propyl-2-bromoisobutyrate and surface-modified silica (SiO₂-Br) were prepared using previously reported procedures. ²⁻⁴ Nitrogen and carbon dioxide gas cylinders (99.99% purity) were obtained from Air Liquide.

Procedures.

Procedures for the synthesis of ionic liquid monomer.

The ionic liquid monomer, 1-(4-vinylbenzyl)-3-butyl imidazolium bis(trifluoromethane) sulfonimides (VBBI⁺ Tf_2N^-) was prepared following previously reported literature.⁵⁻⁷ 4-

Vinylbenzyl chloride was mixed with 1-butylimidazole and acetonitrile. The reaction mixture was stirred at 45 °C for 24 h. The product was precipitated and washed with an excess of ethyl ether and dried in a vacuum at room temperature to give a viscous liquid, 1-(4-vinylbenzyl)-3-butyl imidazolium chloride (VBIC). VBIC was dissolved in deionized water. LiTf₂N was added to the aqueous solution. The reaction continued to stir for 24 h at room temperature. Then, the oil was taken up in ethyl acetate and washed with deionized water. The organic phase was dried over anhydrous MgSO₄ and filtered, and the solvent was removed *via* rotary evaporation. Excess solvent was removed in vacuum to give a very viscous liquid, 1-(4-vinylbenzyl)-3-butyl imidazolium bis(trifluoromethane)sulfonimides (VBBI+Tf₂N-).

Procedures for the preparation of ATRP-initiator-tethered silica particles.

Dry argon gas was bubbled through 50 mL of a dry THF dispersion of the silica particles (15 nm $SiO_2/hollow SiO_2$ nanoparticles, 3.0 g) for 20 minutes then 1.5 mL of 3-(chlorodimethylsilyl)propyl-2-bromoisobutyrate was slowly injected into the dispersion. The reaction was stirred at 60 °C for 24 h, then the flask was cooled down to room temperature and 1.1 mL of hexamethyldisilazane was slowly injected into the reaction. The dispersion was stirred at 35 °C for another 12 h. The modified nanoparticles were dialyzed against methanol three times and acetone twice.



Scheme S1. Functionalization of 15 SiO₂ and hollow SiO₂ nanoparticles by ATRP initiators.

Procedures for the synthesis of polymer grafted SiO₂(hollow SiO₂) particle brushes by ARGET ATRP.

Initiator (SiO₂-Br/hollow SiO₂-Br nanoparticles), monomer (MMA/PEGMEMA, MMA/ionic liquid monomer), solvents (anisole, DMF/BuCN, DMF), CuBr₂, and Me₆TREN, molar ratios shown as a subscript in Table 1, were mixed thoroughly in a sealed Schlenk flask. The mixture was degassed by bubbling with argon. A stock solution of Sn(EH)₂ in anisole was prepared. Then the Sn(EH)₂ solution was injected into the Schlenk flask to activate the catalyst complex and the flask was immediately put into an oil bath set at the desired temperature. The reaction mixture was cooled to room temperature to stop the reactions. SiO₂/hollow SiO₂-*g*-PMMA and SiO₂/hollow SiO₂-*g*-PMMA-*r*-PEGMEMA particle brush reaction mixtures were added to cold methanol to precipitate the product. SiO₂/hollow SiO₂-*g*-PIL particle brushes were soluble and stored in THF.

Procedures for the synthesis of linear PIL homopolymers by ARGET ATRP.

Initiator (EBiB), monomer (ionic liquid monomer), solvents (DMF/BuCN), CuBr₂, and Me₆TREN were mixed thoroughly in a sealed Schlenk flask. The reaction condition is $[IL]_0:[EBiB]_0:[CuBr_2]_0:[Me_6TREN]_0:[Sn(EH)_2]_0=300:1:0.1:1:2$ in 80 vol% butyronitrile, 90 °C. The mixture was degassed by bubbling with argon. A stock solution of Sn(EH)₂ in anisole was prepared. Then the Sn(EH)₂ solution was injected into the Schlenk flask to activate the catalyst complex and the flask was immediately put into an oil bath set at the desired temperature. The reaction mixture was cooled to room temperature to stop the reactions. The reaction mixture was added to cold methanol/water (volume ratio=70:30) to precipitate the product. The final particle brushes were soluble and stored in THF.

Fabrication of polymer/SiO₂ hybrid bulk films by solvent casting.

Rectangular films: Polymer grafted SiO₂/hollow SiO₂ particle brushes were dispersed in THF *via* sonication. After the solution was stirred for 24 h, the bulk dispersions were transferred into 15 mm \times 5 mm rectangular Teflon molds. The solvent was slowly evaporated over 48 h at room

temperature generating homogeneous nanocomposite films with a thickness of 0.1-0.2 mm. The residual solvent was removed from the bulk films by transferring them to a vacuum oven and slowly increasing the temperature at the rate of 10 °C per 24 h to 120 °C. At least five specific bulk films of the same composition were investigated to systematically study the thermomechanical properties of the nanocomposite films.

Round films: Polymer grafted SiO₂/hollow SiO₂ particle brushes were dispersed in THF *via* sonication. After the solution was stirred for 24 h, the bulk dispersions were drop-cast on a Teflon sheet. The solvent was slowly evaporated over 24 h at room temperature generating homogeneous nanocomposite films with a thickness of 0.3-0.6 mm. 10 diameters round films were punched for gas transport test. The residual solvent was removed from the bulk films by transferring them to a vacuum oven and slowly increasing the temperature at the rate of 10 °C per 24 h to 120 °C.

Characterization.

Size Exclusion Chromatography (SEC). Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by SEC. The SEC of PMMA and PMMA-*r*-PEGMEMA was conducted with a Waters 515 pump and a Waters 410 differential refractometer with PSS columns (Styrogel 105, 103, and 102 Å) in THF as an eluent at 35 °C and a flow rate of 1 mL min⁻¹. Linear PMMA standards were used for calibration. SEC measurements of polyVBBI⁺Tf₂N⁻ were performed with THF containing 10 mM LiTf₂N and 10 mM 1-butylimidazole as the eluent.⁷

Porous Structure Study. The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini 2360 surface area analyzer. The samples were outgassed at 200 °C for 16 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using the non-local density functional theory (NLDFT) method.

Nuclear Magnetic Resonance (NMR). The composition of SiO₂/hollow SiO₂-*g*-PMMA-*r*-PEGMEMA particle brushes was characterized by ¹H NMR with a Bruker Advance 400 MHz NMR spectroscopy in CDCl₃ solvent.

Transmission Electron Microscopy (TEM). TEM was carried out using a JEOL NEOARM electron microscope operated at 200 kV to characterize the morphology and structure of the polymer grafted SiO₂/hollow SiO₂ particle brushes, samples were dropped cast onto a carbon-coated copper grid. The spatial distribution, radius, and inter-particle distances of the SiO₂/hollow SiO₂ nanoparticles were determined from statistical analysis of the TEM micrographs using ImageJ software.

Dynamic Light Scattering (DLS). DLS was carried out on an ALV compact goniometer system with a 7002 Multiple Tau Digital Correlator to determine intensity-weighted average hydrodynamic radius and distribution. The polymer grafted 15 nm SiO₂ and hollow SiO₂ particle brushes were suspended in filtered THF (450 nm PTFE filter) at low concentrations (1 mg mL⁻¹). **Thermogravimetric Analysis (TGA).** TGA with TA Instruments 2950 was used to measure the fraction of SiO₂ in the polymer grafted SiO₂ (hollow SiO₂) particle brushes. The data were analyzed with TA Universal Analysis. The heating procedure involved four steps: (1) jump to 120 °C; (2) hold at 120 °C for 10 min; (3) ramp up at a rate of 20 °C/min to 800 °C; (4) hold for 2 min. The TGA plots were normalized to the total weight after holding at 120 °C.

Differential scanning calorimetry (DSC). The glass transition temperature (T_g) of polymer grafted SiO₂ (hollow SiO₂) particle brushes were measured by differential scanning calorimetry (DSC) with TA Instrument QA-100. The same procedure was run three times, each involving the following steps: (1) Equilibrate at 25.00 °C, (2) Isothermal for 1.00 min, (3) Ramp 20.00 °C/min to -90.00 °C, (4) Isothermal for 1.00 min, (5) Ramp 20.00 °C/min to 150.00 °C, (6) Isothermal for 1.00 min, (7) Ramp 20.00 °C/min to -90.00 °C, (8) Isothermal for 1.00 min, (9) Ramp 20.00 °C/min to 150.00 °C, (10) Isothermal for 1.00 min, (11) Ramp 20.00 °C/min to -90.00 °C, (12) Isothermal for 1.00 min, (13) Ramp 20.00 °C/min to 150.00 °C, (14) Isothermal for 1.00 min, (15) Jump to 25.00 °C. The DSC data were analyzed with a TA Universal Analysis instrument, and T_g was directly acquired.

Mechanical Analysis. The polymer grafted SiO₂/hollow SiO₂ particle brushes bulk films are tested in the tensile mode by using an RSA-G2 solid analyzer (TA Instruments). The film thickness was between 60-100 μ m. The samples were stretched at a constant crosshead velocity of 0.005 mm/s at room temperature.

Gas Permeation Measurements. To experimentally determine the permeability of the polymer graft SiO₂ particle brush hybrid films, a custom-built testing apparatus was used to record the single gas permeation measurements.⁸⁻⁹ The permeability of a membrane is a quantification of the analyte's ability to pass through the membrane medium and is calculated using the gas flux through a specific membrane thickness over a certain pressure drop. The selectivity represented here is defined as the ratio of permeabilities of the more permeable species (CO₂) versus the less permeable species (N₂) also known as the perm selectivity.

Pure/single gas (CO₂ or N₂) transport test was carried out at a temperature of 25 °C and feed pressure of 35 kPa. The membrane sample was mounted on an aluminum foil with a hole at the center. The hole was created by a power punch with a diameter of 8 mm. The sample was sandwiched and sealed between the Swagelok VCR fittings. The test chamber is configured with the membrane separating the gaseous feed cell from the permeate cell. Before analysis, membranes were inserted into the sample chamber and placed under vacuum to outgas and equilibrate. The pressure rise was monitored using a 10-Torr Baratron gauge. From the slope of this pressure rise, the permeability was calculated based on the equation: $P = \frac{Vl}{RTA(\Delta p)d_t} d_p$ where V is the permeate volume, l is the membrane thickness, R is the gas constant, T is the absolute temperature, A is the membrane area, Δp is the pressure difference across the membrane and d_p/d_t is the rate of gas pressure increase on the permeate side. The pressure measurement from the Baratron gauge is independent of gas composition and has a range of up to 100 Torr. The pressure on the permeate side was typically measured for 30 minutes. All samples were tested 4 times to get the average values with error bars.

Determining the initiating site density for SiO₂-Br nanoparticles. The concentration of initiating sites on the surface of silica nanoparticles was determined by model reactions (i.e. polymerization of SiO₂-g-PMMA, [MMA]₀/[SiO₂-Br]₀/[CuBr₂]₀/[Me₆TREN]₀/[Sn(EH)₂]₀ = 2000:1:1:10:8 with 45 vol% anisole, 5 vol% DMF at 60 °C) with a certain amount of SiO₂-Br nanoparticles (e.g. 100 mg). After purification, SEC and TGA were conducted to characterize the grafting density of the particle brushes. The particles used in the current study had grafting density (σ_0) ~ 0.40 nm⁻², the -Br (initiating site) concentration on the surface was assumed the same. Based on the average radius of nanoparticles, 7.9 nm, density of silica, 2.2 g/cm³, the average molar mass of 15 nm SiO₂-Br nanoparticles, is 8,720 g/mol.

15 nm Particle Brush Grafting Density Calculation.

The grafting density was calculated using the formula (S1).

$$\sigma_{\mathrm{TGA}} = \frac{(1 - f_{\mathrm{SiO2}})N_{\mathrm{Av}}\rho_{\mathrm{SiO2}} d}{6 f_{\mathrm{SiO2}} M_n}$$
(S1)

where f_{SiO2} is the SiO₂ fraction measured by TGA, N_{Av} is the Avogadro number, ρ_{SiO2} is the density of SiO₂ nanoparticles (2.2 g/cm³), *d* is the average diameter of SiO₂ nanoparticles (15.8 nm), M_n is the overall number-average MW of the cleaved polymer brushes.

SiO₂-g-PMMA: 0.33 chains/nm²

SiO₂-g-PMMA-r-PEGMEMA: 0.41 chains/nm²

SiO₂-g-PIL: 1.3 chains/nm²

Supporting data:



Figure S1. TEM images of (a) 15 nm SiO_2 -Br nanoparticle, (b) hollow porous SiO_2 -Br nanoparticles with average particle size around 60 nm. Scale bars: 200 nm.



Figure S2. (a-b) comparison of N_2 adsorption/desorption isothermal of functionalized hollow SiO₂-Br nanoparticles (red) and 15 nm SiO₂-Br nanoparticles (black), (c-d) pore size distribution of functionalized hollow SiO₂-Br nanoparticles (red), and 15 nm SiO₂-Br nanoparticles (black).



Figure S3. SEC traces of 15 nm SiO₂ and hollow SiO₂ particle brushes: (a) SiO₂-*g*-PMMA, (b) SiO₂-*g*-PMMA-*r*-PEGMEMA, (c) SiO₂-*g*-PIL, (d) hollow SiO₂-*g*-PMMA, (e) hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-*g*-PIL.



Figure S4. NMR spectrum of (a) SiO_2 -*g*-PMMA-*r*-PEGMEMA and (b) hollow SiO_2 -*g*-PMMA-*r*-PEGMEMA particle brushes. The spectrums show the PMMA/PEGMEMA molar fraction in 15 nm solid silica particle brush is 55%/45% and in hollow silica particle brush is 59%/41%.



Figure S5. TGA curves of 15 nm SiO₂ and hollow SiO₂ particle brushes: (a) SiO₂-*g*-PMMA, (b) SiO₂-*g*-PMMA-*r*-PEGMEMA, (c) SiO₂-*g*-PIL, (d) hollow SiO₂-*g*-PMMA, (e) hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-*g*-PIL.



Figure S6. DSC curves of 15 nm SiO₂ and hollow SiO₂ particle brushes: (a) SiO₂-*g*-PMMA, (b) SiO₂-*g*-PMMA-*r*-PEGMEMA, (c) SiO₂-*g*-PIL, (d) hollow SiO₂-*g*-PMMA, (e) hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-*g*-PIL.



Figure S7. Size distribution of polymer grafted 15 nm SiO₂ and hollow SiO₂ particle brushes measured by DLS in THF solution: (a) SiO₂-*g*-PMMA, (b) SiO₂-*g*-PMMA-*r*-PEGMEMA, (c) SiO₂-*g*-PIL, (d) hollow SiO₂-*g*-PMMA, (e) hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-*g*-PIL. Intensity-average particle brush size: SiO₂-*g*-PMMA, 146 nm; SiO₂-*g*-PMMA-*r*-PEGMEMA, 92 nm; SiO₂-*g*-PIL, 116 nm; hollow SiO₂-*g*-PMMA, 487 nm; hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, 353nm; hollow SiO₂-*g*-PIL, 242 nm.



Figure S8. Photographs of polymer grafted SiO₂/hollow SiO₂ particle brush bulk films, film size: 15×5 mm with thickness ~ 100 to 200 μ m: (a) SiO₂-g-PMMA, (b) SiO₂-g-PMMA-*r*-PEGMEMA, (c) SiO₂-g-PIL, (d) hollow SiO₂-g-PMMA, (e) hollow SiO₂-g-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-g-PIL.



Figure S9. Strain-stress curves of polymer grafted 15 nm SiO₂ and hollow SiO₂ particle brushes: (a) SiO₂-*g*-PMMA, (b) SiO₂-*g*-PMMA-*r*-PEGMEMA, (c) SiO₂-*g*-PIL, (d) hollow SiO₂-*g*-PMMA, (e) hollow SiO₂-*g*-PMMA-*r*-PEGMEMA, (f) hollow SiO₂-*g*-PIL.



Figure S10. (a) Strain-stress curves of linear PIL homopolymers with M_n =23,270, M_w/M_n =2.51, (b) Young's modulus values for PIL homopolymer and solid/hollow silica particle brushes, (c) Photographs of linear PIL homopolymer bulk films, film size: 15×5 mm with thickness ~ 100 to 200 μ m.

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